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The Effects of Electrolytes upon the Rate of Drying of Tennessee Ball Clay No. 7

Ceramic Engineering

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THE EFFECTS OF ELECTROLYTES UPON THE RATE OF DRYING OF TENNESSEE BALL CLAY

No. 7

BY

THOMAS NEWKIRK McVAY

THESIS

FOR THE

DEGREE OF BACHELOR OF SCIENCE

IN

CERAMIC ENGINEERING

COLLEGE OF LIBERAL ARTS AND SCIENCES

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June 1st 1914

THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

Thomas Newkirk McVay

ENTITLED The Effect Of Electrolytes Upon The Rate Of Drying Of Tennessee Ball Clay No. 7

IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

DEGREE OF Bachelor of Science in Ceramic Engineering

R. T. Stull
Instructor in Charge

APPROVED: R. T. Stull

HEAD OF DEPARTMENT OF Ceramics.

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The Effects of Electrolytes Upon the Rate of Drying of Tennessee Ball Clay.

Forms of Colloids— The colloids found in clay slips may exist in two characteristic forms (1) as a homogeneous suspension in a liquid in the form of a "sol" and (2) as a continuous jelly with pore walls and pores filled with a liquid and called a "gel". Solids are included under (2) as a limiting case.[1]

When "gels" or "sols" are in water suspension they are known as hydrogels or hydrosols, when in alcohol as alcosols,etc.

There is also an independent classification of colloids ie, reversible and irreversible. The former are those colloids which when coagulated, can be made to return to their original condition, while the latter will not so revert. The passing from sol to gel is called "coagulation" that from gel to sol,"peptinization". But when granular matter is present, Ashley prefers the terms flocculation for the former and deflocculation for the latter.

Irreversible colloids carry an electric charge and are quickly coagulated by the addition of electrolytes, carrying an opposite charge, while the reversible ones are not so affected. The irreversible hydrosol changes into a hydrogel or separates from the liquid in a gelatinous or amorphous condition. Hardy's [2]

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1. Ashley,Bull. 388 U. S. Geological Survey
2. Hardy W.B., Mechanism of Gelatines in Reversible Colloidal Systems.

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classification of reversible or irreversible colloids is based on whether the dried residue is soluble or insoluble in the solvent employed. Pöschl[3] remarks that all aqueous solutions in coagulation are not homogeneous, some leave behind an aqueous residue, others an insoluble one. Zsigmondy[4] mentions the following as examples of the two classes: Reversible; dextrine, gum arabic, albumins, molybdic and molybdic oxide; Irreversible; stannic acid, many colloidal oxides and sulphides. Ramann[5] mentions clay hydrate, hydrated silic acid and ferric hydroxide.

The question in the case of clay is whether it can be classed as irreversible or not, although very sensitive to electrolytes. When the flocculating agent is washed out, deflocculation takes place. Also the coagulating effect of $MgSO_4$ [6] may be partly neutralized by NA_2CO_3. Thus a classification of clay as irreversible based on the effect of electrolytes will not hold. Although according to Hardy's classification based on the solubility of the dried residue clay would be classed as irreversible.

Ashley [1] remarks that with few exceptions, clays represent the amorphous or colloidal appearance, any crystalline matter present being largely marked by a coating of colloidal matter.

He gives the following comprehensive definition for

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3. Pöschl, Chemistry of Colloids

4. Zsigmondy, Colloids and the Ultra-Miscroscope

5. Ramann, Colloidal Studies in Soil Work

6. R. Riecke, Sprechsaal Kalender thru Pottery Gazette 38-1153

clays : "A mixture of minerals of which the most prominent members are silicates of aluminum, iron, the alkalies and alkaline earths."

Kaolin (Al_2O_3, 2 SiO_2, $2H_2O$) is the principal constituent of pottery clays, being the final product of the breaking down of feldspar. The kaolin may show crystal faces but usually the faces are irregular. These grains are usually coated with a colloid, the colloidal substance being a hydrous silicate, iron, manganese and aluminum hydroxides, or organic colloidal matter. Quartz and mica grains have this coating to a less degree.

Schlaesig[7] in 1874 made an examination of a number of clays and isolated the colloids, thus proving that clays are colloidal.

Ashley [1] summarizes this discussion on the colloidal matter in clays as follows: "The colloidal matter in clays are therefore non-crystalline, hydrated gelatinous aluminum silicates, organic colloids , gelatinous silic acid and hydrated ferric oxide. Rarely there may be present aluminum hydrate.

Effect of Electrolytes on Viscosity- According to Ashley[1] most of the colloidal matter in very plastic clay is in hydrogel condition, very little in the hydrosol form. Such clays in their natural beds have enough dissolved salts, i.e. $CaSO_4$ to keep them coagulated. Clays not coagulated have very little adhesive and cohesive properties.

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[7] Comp. Rend Vol. 79, 1874, pp. 376-380, 473-477. Thru Bull. #388, U. S. Geological Survey

Rohland [8] makes very definite statement as regards plasticity and states that the real reason for plasticity is that clays in the air dried state contain substances in the colloidal condition, and forms hydrogels in contact with water and further that these substances in the colloidal state possess plastic properties. He explains that the plasticity of a given clay depends on the amount of hydroxyl ions present in water. When this is large the negatively charged clay particles will go into suspension. When the hydroxyl concentration is depressed as by the addition of acids or depression of temperature, the clay will assume the gel condition and become plastic.

Rohland formulated a set of rules for decreasing plasticity "For decreasing plasticity may be used all bases, organic and inorganic, all salts of strong bases with weak acids which hydrolytically split off OH ions in large amounts. To this group belong potash, soda, salts of phosphoric acids and salts of silic acid". He concludes that neutral salts appear to behave indifferently as NaCl, NA_2SO_4, KnO_3 etc.

Hardy[2] agrees that a sol is coagulated when its static charge is neutralized. Ashley[1] further explains that the positive ion is the most effective in causing the precipitation or the coagulation, the acid ion taking little part.

The power seems to vary but little with different positive ions of the same value. Ashley gives figures to show that the trivalent ion has sixty times the power of the monovalent and

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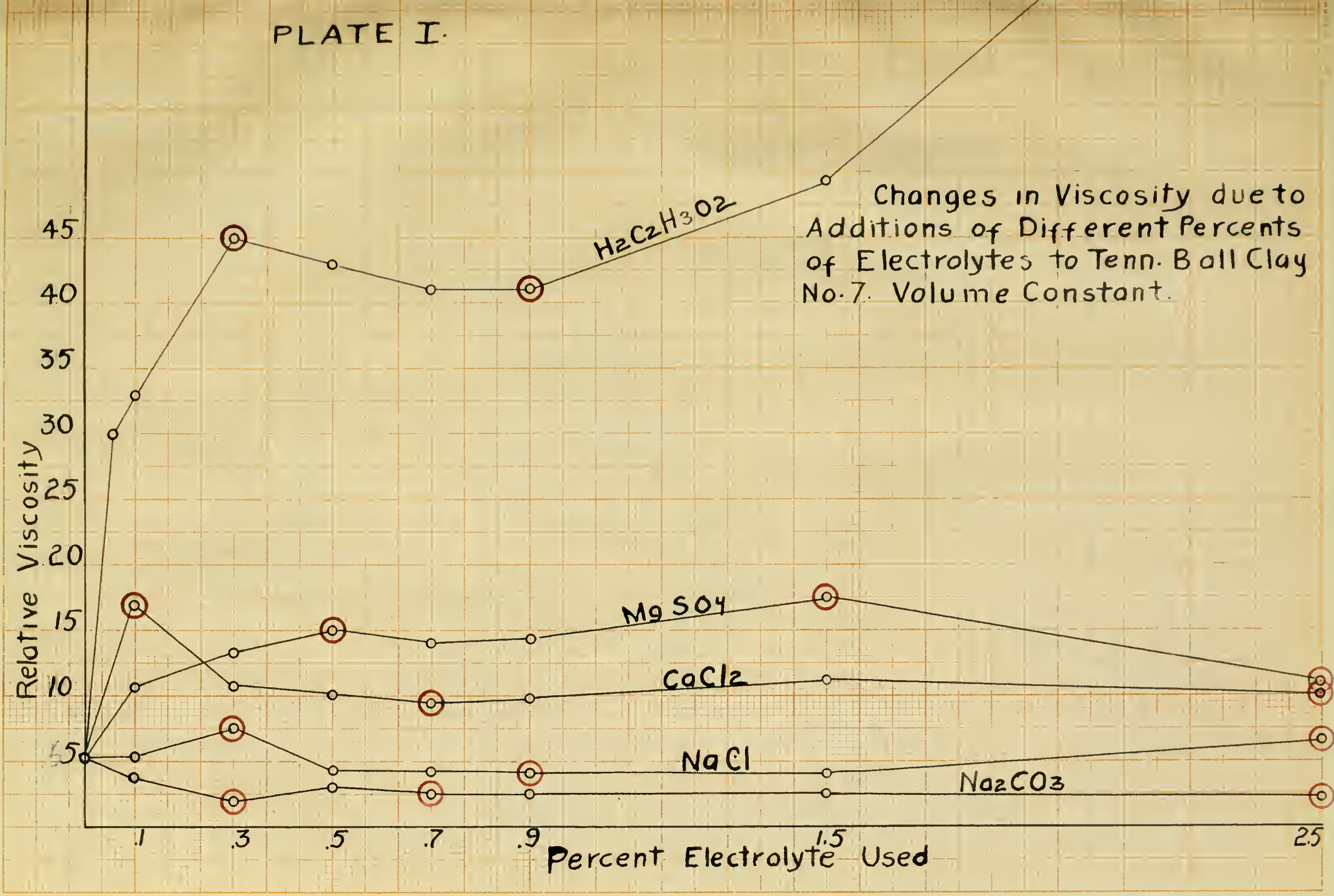
[8] Rohland, The Colloidal and Crystalloidal State of Matter.

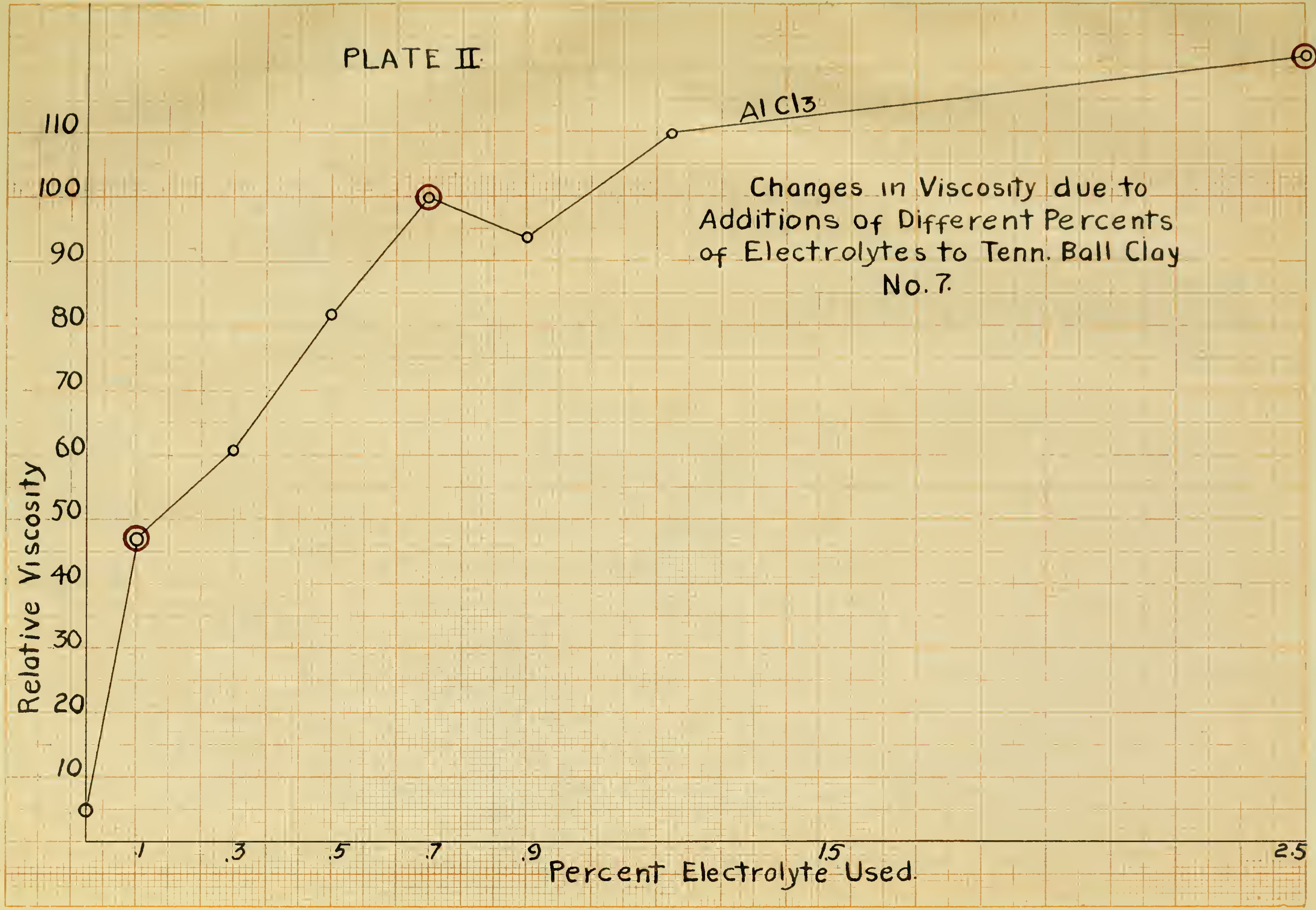
PLATE I.



Changes in Viscosity due to Additions of Different Percents of Electrolytes to Tenn. Ball Clay No. 7. Volume Constant.

[illegible]

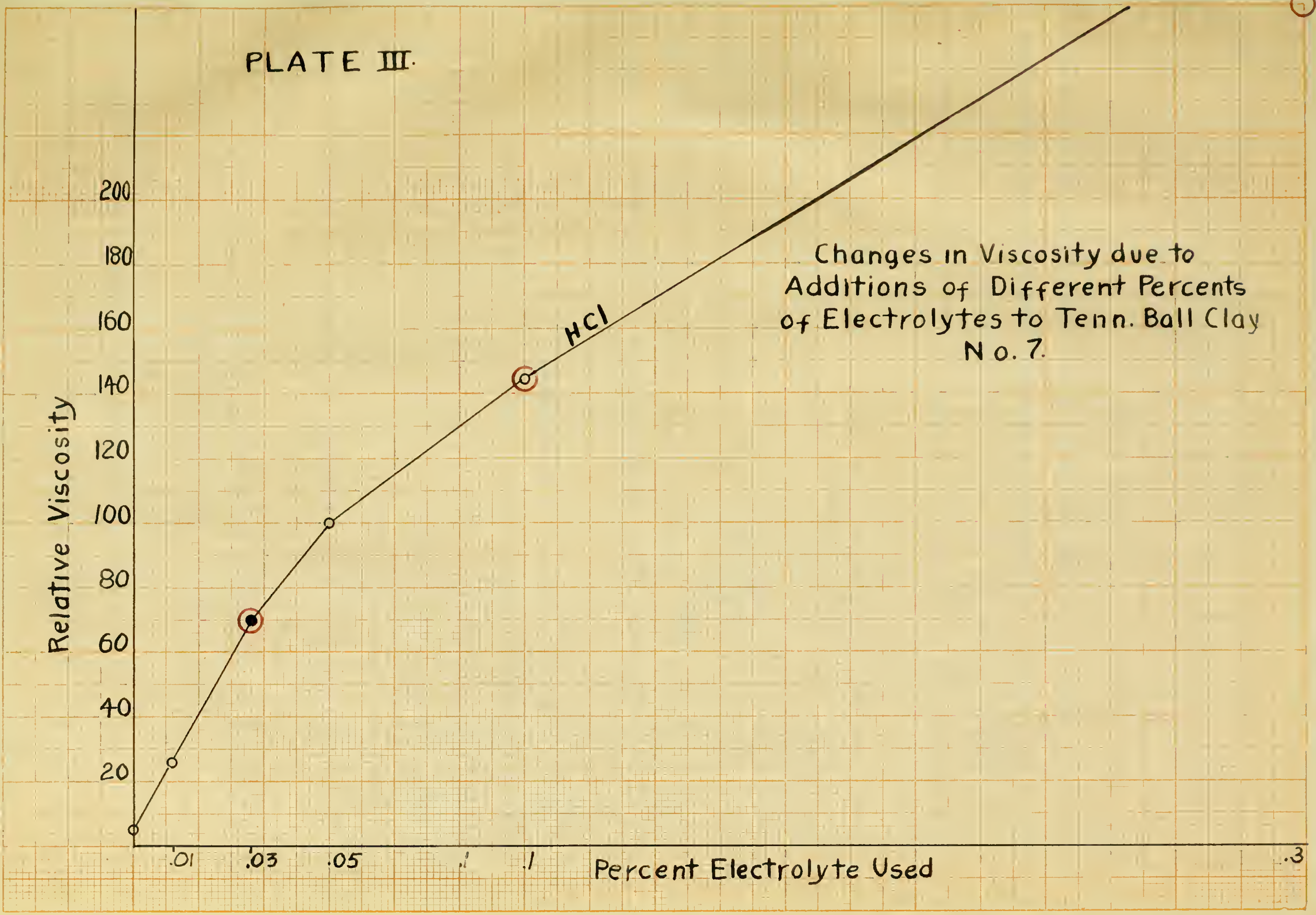
PLATE II.



Changes in Viscosity due to Additions of Different Percents of Electrolytes to Tenn. Ball Clay No. 7.

[illegible]
[illegible]
[illegible]

PLATE III.



Changes in Viscosity due to Additions of Different Percents of Electrolytes to Tenn. Ball Clay No. 7.

[illegible]

the trivalent six hundred times that of the monovalent

The theory of coagulation is also based on electrostatic laws. According to this theory coagulation occurs when the ions added or already present attract to themselves the particles in the colloidal state carrying opposite electric charges. They form complexes with them which gradually sink to the bottom. But when ions and colloidal particles of the same charge meet, a repulsion of the particles occurs so that the colloidal state is maintained.

There is another cause for coagulation besides the one given above, due to the removal of the water of the colloid by such electrolytes as $CaCl_2$, $AlCl_3$, and $FeCl_3$. These have high affinity for water and readily hydrate. The water of the colloids may amount to 5 - 10 percent of the total, when the colloidal envelope is destroyed and the suspended granular matter settles or coagulates.[1]

VISCOSITY

A measure of relative viscosity may be used as a means to determine the degree of coagulation or deflocculation of clays. It has been shown that the causes of coagulation and deflocculation are due to the influence of electrolytes upon the colloids in clay. Different electrolytes added to clay slips produce different results.

Rohland [8] found that neutral salts behaved indifferently and also the work of Ashley supports his conclusions.

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[1] Ashley, Bull. 388 U. S. Geological Survey

[8] Rohland, The Colloidal and Crystalloidal State of Matter.

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Masoni[9] remarks that chlorides have greater coagulating effects than the sulphates. Riecke[6] formulated a set of rules for the effects of sulphates.

> " 1. Soluble sulphates when added in small quantities to clay slips increase their viscosity $CuSO_4$, $Al_2(SO_4)_3$ and sulphates of heavy metals are the most effective.
> 2. All sulphates have a stiffening effect when added in small amounts, slightly larger amounts produce liquefaction, but still larger amounts cause a further increase in viscosity.
> 3. The efficiency expressed as the ratio of the increased viscosity to the original viscosity increases considerably in all cases when the amount of added sulphates is small, but with larger amounts may diminish."

The effect of Na_2CO_3 as a deflocculator is very interesting. Neubert[10] did work to ascertain the cause of the liquefaction of clays. He comcludes - "The effect of alkalies are closely

> connected with the presence in clays of humic substances in the form of dried gel, in a very fine state of subdivision. When the clay is brought in contact with an alkali solvent, the clay particles adsorb OH ions and in consequence of the electric charge thus acquired repel one another, thus causing the mixture to appear more liquid. This effect is opposed by stiffening action produced by the swelling of the clay particles and rises to a maximum with still higher concentrations of alkali; the clay particles are coagulated which results in stiffening but gradually the alkali dissolves the humic substances, and thus induces the further subdivision of the clay particles, while the alkali humates act as a protective colloid and hide the segregation of the particles of colloids. This is the cause of the so-called 'reliquefaction', of the fact that when a greater concentration of alkali is added than necessary to produce maximum liquefaction, the mixutre first becomes stiffer but on standing becomes less viscous."

Viscosity is only one of the changes in the physical state caused by the addition of electrolytes, another very important one is the drying shrinkage.

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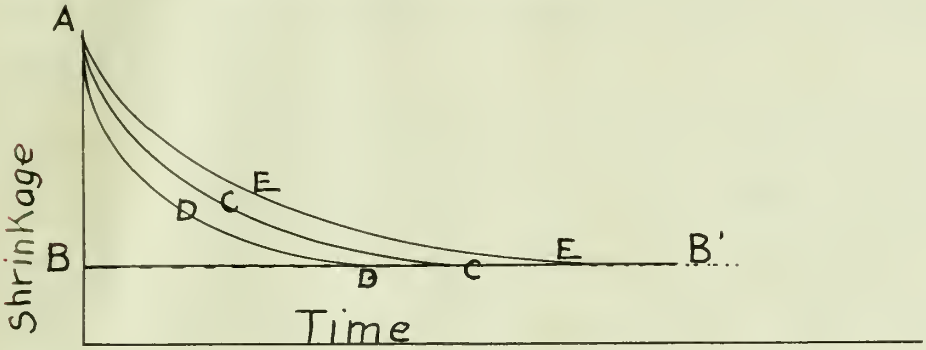
[9] Masoni Staz. Spec. Agr. Ital.

[10] Neubert, J. R. Sprechsaal 46-523-4

Bleininger [11] found that the effect of coagulators, i.e. Hcl, decreased the total drying shrinkage and that the addition of deflocculators increased it, which is opposite to the work done by Rohland, since he considered drying shrinkage a measure of the plasticity. Bleininger did not attempt to explain this phenomena. Although the total drying shrinkage is very important in the fitting of bodies and clay slips or engobes, the rate of drying is of equal importance.



Suppose the ordinate AB represents the total volume shrinkage and the abscissa BB' represents the time.

ACB' = Drying curve of the body. Now if AD represents the drying curve of the slip, and the slip, although having the same total shrinkage, the rate of drying is faster than the body and cracking will result. If the rate of drying of the slip is slower than that of the body i.e. the curve AE, then flaking will result. Thus a control of the rate of shrinkage is useful in practical work. As no work (as far as I could ascertain) has been done upon this subject, work was done to find out if the rate of drying could be controlled by the addition of electrolytes, since they exercise great influences upon the physical properties of clays.

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11. Bleininger, Bull. No. 17 Dept. Cer. U. of I.

The manipulations for the experiments were as follows:

PREPARATION

Tennessee Ball Clay No. 7 was made into a slip by blunging the raw clay in a ball mill with distilled water. After a homogeneous slip was prepared, slip equivalent to 25 grams of dry clay was carefully weighed into jars, which had been thoroughly cleansed in distilled water and then dried, water and electrolytes were then added to make a volume of 130 cc. of solution for each sample of clay.

The slips were run through a modified form of the tube viscosimeter which had been previously standardized with water. The mean of several readings was taken, this result being used in plotting the curve. The relative viscosity as plotted on the ordinate (Plate 1, 2, 3) =

$$\frac{\text{Time in seconds for slip to run through the viscosimeter}}{\text{Time in seconds for water to run through the viscosimeter}}$$

The solutions of electrolytes were made up by dissolving the C. P. chemicals in distilled water and various methods of standardizations were employed. $CaCl_2$ and $AlCl_3$ solutions were analyzed. Hcl and $H_2C_2H_3O_2$ solutions were made by mixing the standard C. P. acids with distilled water in a volimetric flask. The $MgSO_4$ solution was standardized by drying 25 cc. in a casserole ignited to 200° C. (in order to remove chemical water) cooled in a dessicator and weighed.

The Na_2CO_3 and NaCl were standardized by drying 25 cc. in a casserole at 100° C., cooled as before and weighed.

From the viscosity curves Max. and Min. points were taken,

also other conspicuous points, besides the Max. amount of electrolyte used. (Points are denoted by red circles on PLATES 1, 2,3). These different amounts of electrolytes were added to distilled water to make 40 cc. of solution for each 100 grams of the dry clay. The bodies were thoroughly wedged and placed in a wet can for twenty four hours. Two briquettes being made up of each body and placed on glass plates which had been previously weighed. Pins were stuck in the briquettes in order to measure shrinkage. The briquettes were again placed in a wet can for twenty four hours and were then weighed on fine balances to .01 grams, the distances between the pins being measured with micrometer calipers.

These briquettes were dried gradually by admitting air into the wet can and frequently changing the position of the clay bars on the pallet, in order that all would be subject to equal drying conditions. They were weighed and measured every other day until the 16th day when loss of water and shrinkage had practically ceased.

They were then dried four days in the open air, weighed and measured again, then dried four hours at 100° C. and the dry lengths and weights taken.

The percentage water loss and shrinkage (based on dry weight and dry length) were calculated for each day and the results plotted.

CONCLUSIONS

The viscosity curves (PLATES 1, 2, 3) corroborate results found by other writers. As no new results were discovered it is not necessary to go into further detail as to the flocculation and deflocculation of clays.

PLATE IV.

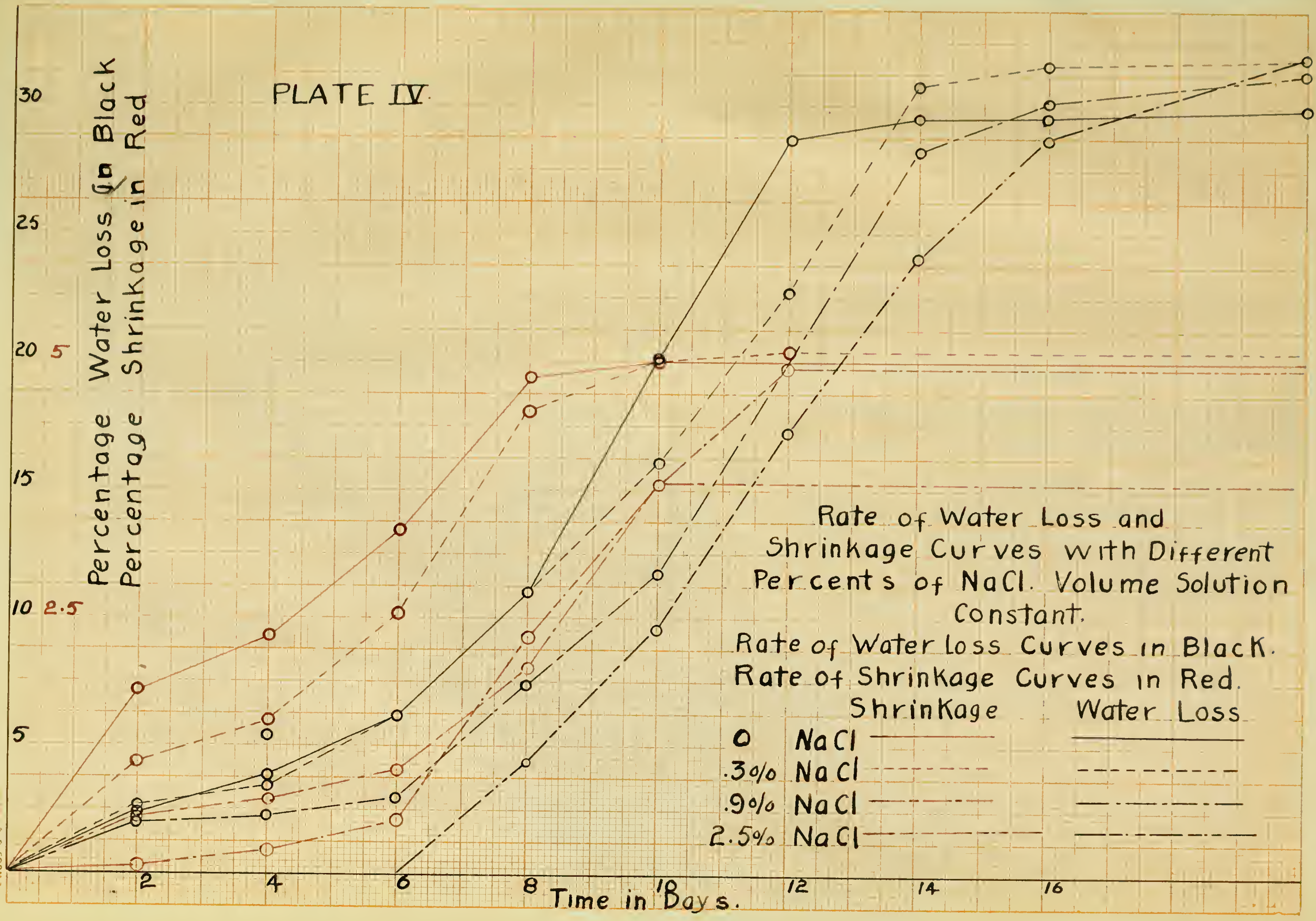
Rate of Water Loss and Shrinkage Curves with Different Percents of NaCl. Volume Solution Constant.
Rate of Water loss Curves in Black.
Rate of Shrinkage Curves in Red.
Shrinkage
Water Loss
0 NaCl
.3% NaCl
.9% NaCl
2.5% NaCl
Percentage Water Loss in Black
Percentage Shrinkage in Red
30
25
20 5
15
10 2.5
5
2
4
6
8
10
12
14
16
Time in Days.

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PLATE V

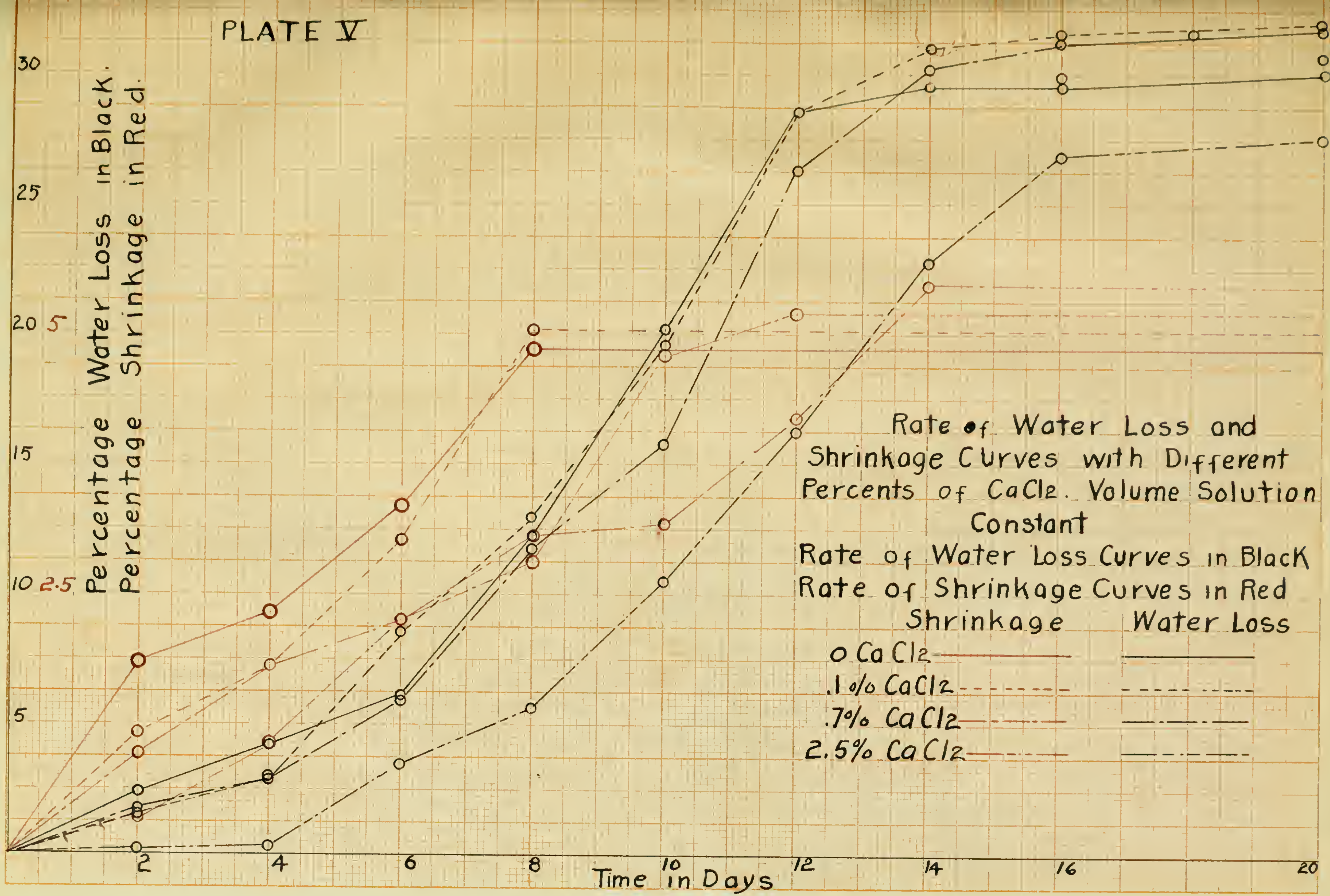
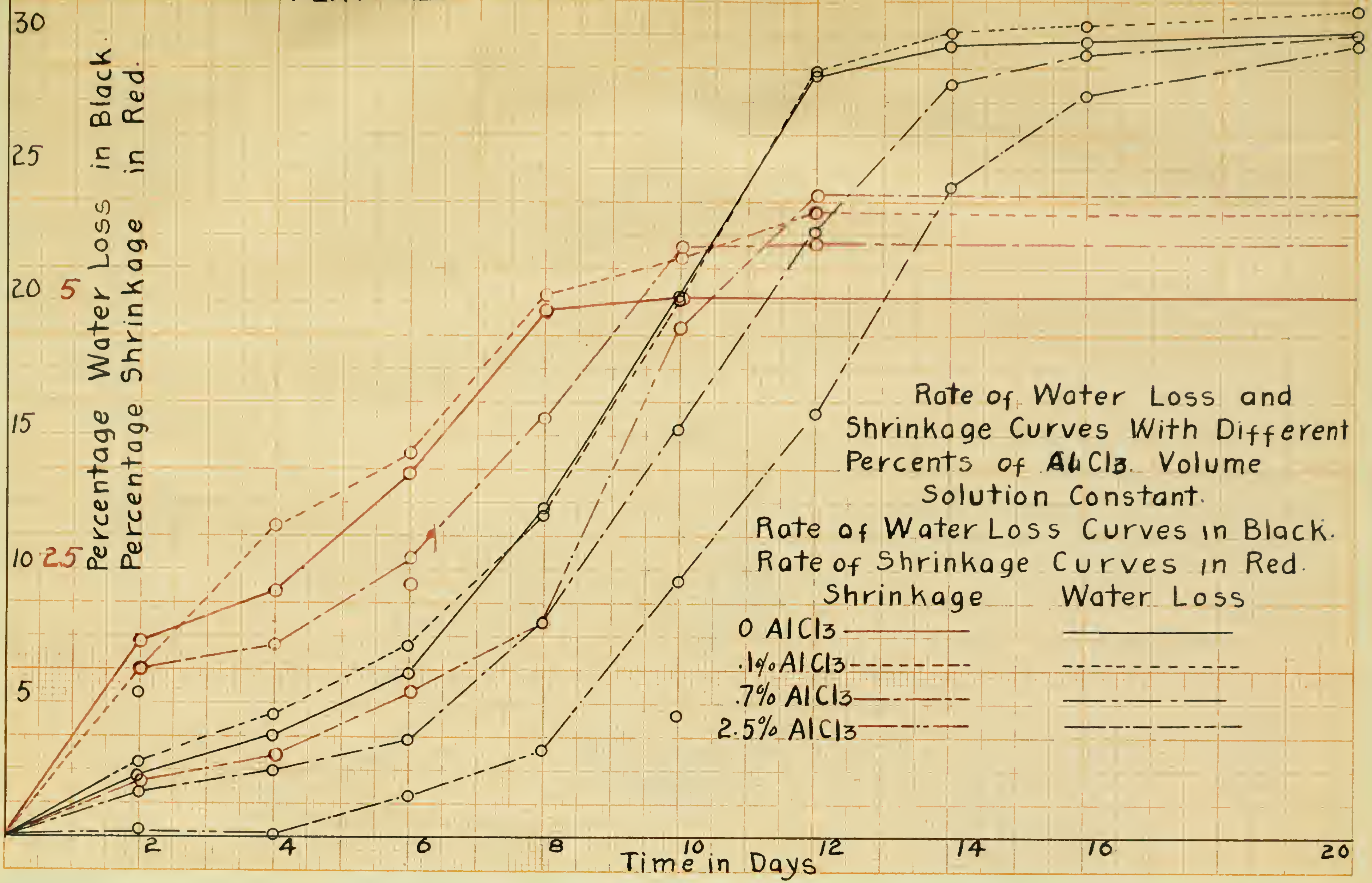
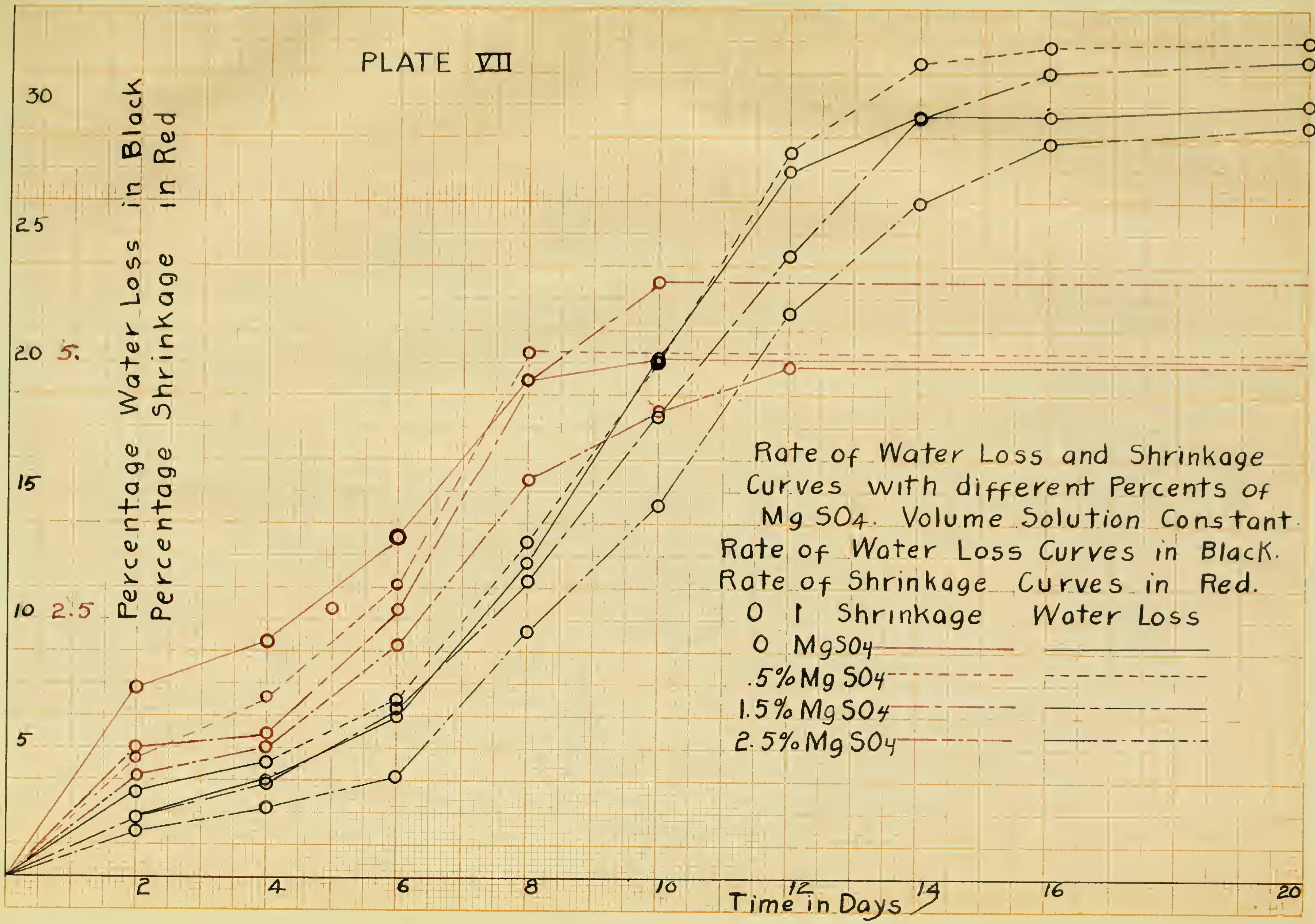

Rate of Water Loss and Shrinkage Curves with Different Percents of $CaCl_2$. Volume Solution Constant
Rate of Water Loss Curves in Black
Rate of Shrinkage Curves in Red
Shrinkage
Water Loss
0 $CaCl_2$
.1% $CaCl_2$
.7% $CaCl_2$
2.5% $CaCl_2$
Percentage Water Loss in Black.
Percentage Shrinkage in Red.
30
25
20 5
15
10 2.5
5
2
4
6
8
10
12
14
16
20
Time in Days

PLATE VI


Rate of Water Loss and Shrinkage Curves With Different Percents of AlCl3. Volume Solution Constant.
Rate of Water Loss Curves in Black.
Rate of Shrinkage Curves in Red.
Shrinkage
Water Loss
0 AlCl3
.1% AlCl3
.7% AlCl3
2.5% AlCl3
Percentage Water Loss in Black.
Percentage Shrinkage in Red.
30
25
20
15
10
5
5
2.5
Time in Days
2
4
6
8
10
12
14
16
20

[illegible]

PLATE VII



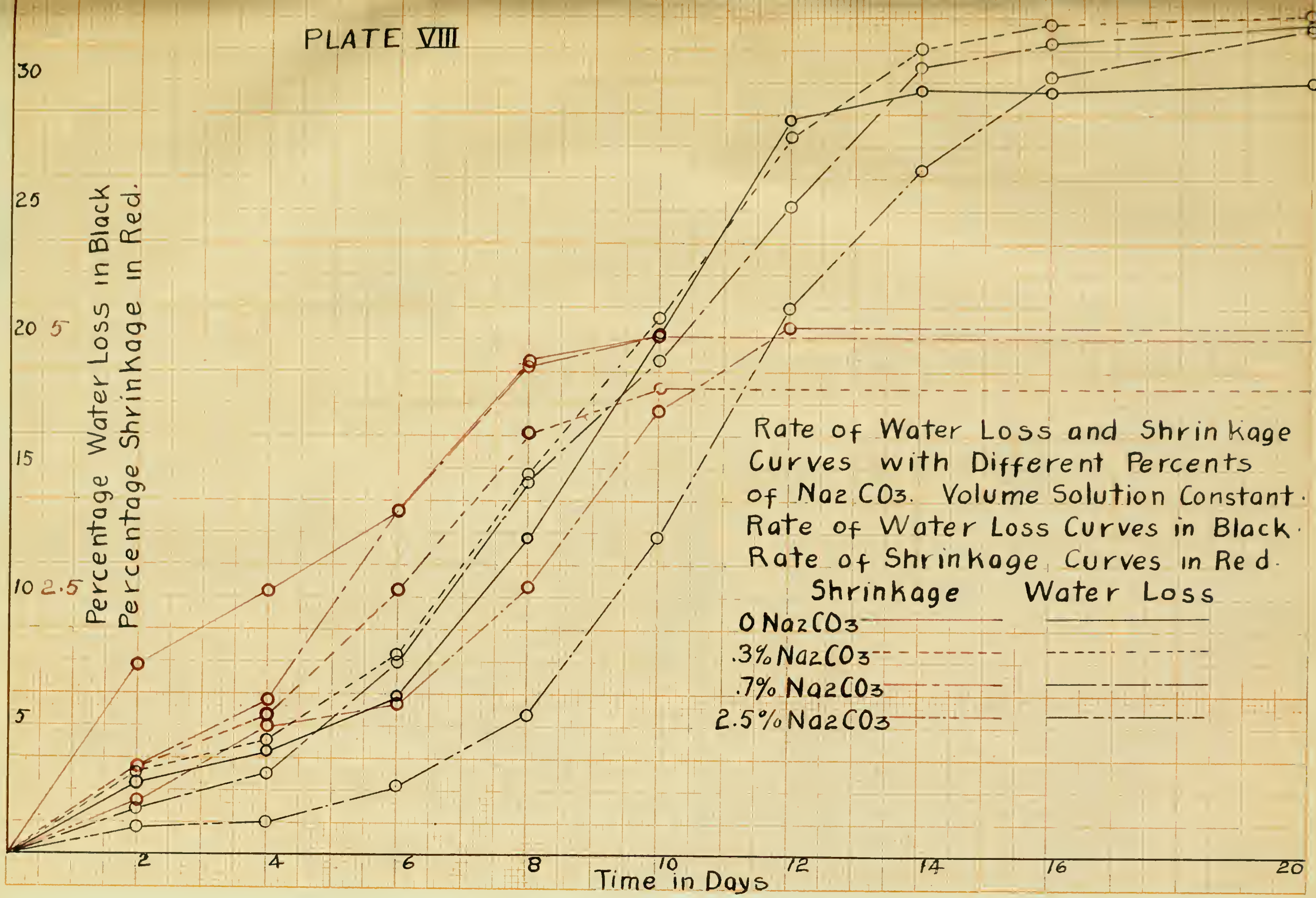
Rate of Water Loss and Shrinkage Curves with different Percents of Mg SO4. Volume Solution Constant.

Rate of Water Loss Curves in Black.

Rate of Shrinkage Curves in Red.

[illegible]
[illegible]

PLATE VIII


30
25
20 5
15
10 2.5
5
Percentage Water Loss in Black
Percentage Shrinkage in Red.
2
4
6
8
10
12
14
16
20
Time in Days
Rate of Water Loss and Shrinkage Curves with Different Percents of Na_2CO_3. Volume Solution Constant.
Rate of Water Loss Curves in Black.
Rate of Shrinkage Curves in Red.
Shrinkage
Water Loss
0 Na_2CO_3
.3% Na_2CO_3
.7% Na_2CO_3
2.5% Na_2CO_3

[illegible]

Because of the movement of the pins when the briquettes were wet it is impossible to get an accurate measure of the total shrinkage although, he rate of shrinkage measurements are very uniform in results. Bleininger[11] investigated total shrinkage of clays by using a volume nometer (Linear measurements not being sufficiently sensitive), but this would not be practical when shrinkage measurements are to be taken every day, except that a large number of briquettes be made.

From the curves (PLATES 4, 5, 6, 7, 8) we find that the addition of soluble salts decreased the rate of water loss and also the drying shrinkage, independent of whether the amount used caused Max. or Min. viscosity.

The addition of soluble salts decreased the rate of water loss and shrinkage independent of whether the salts were flocculators or deflocculators.

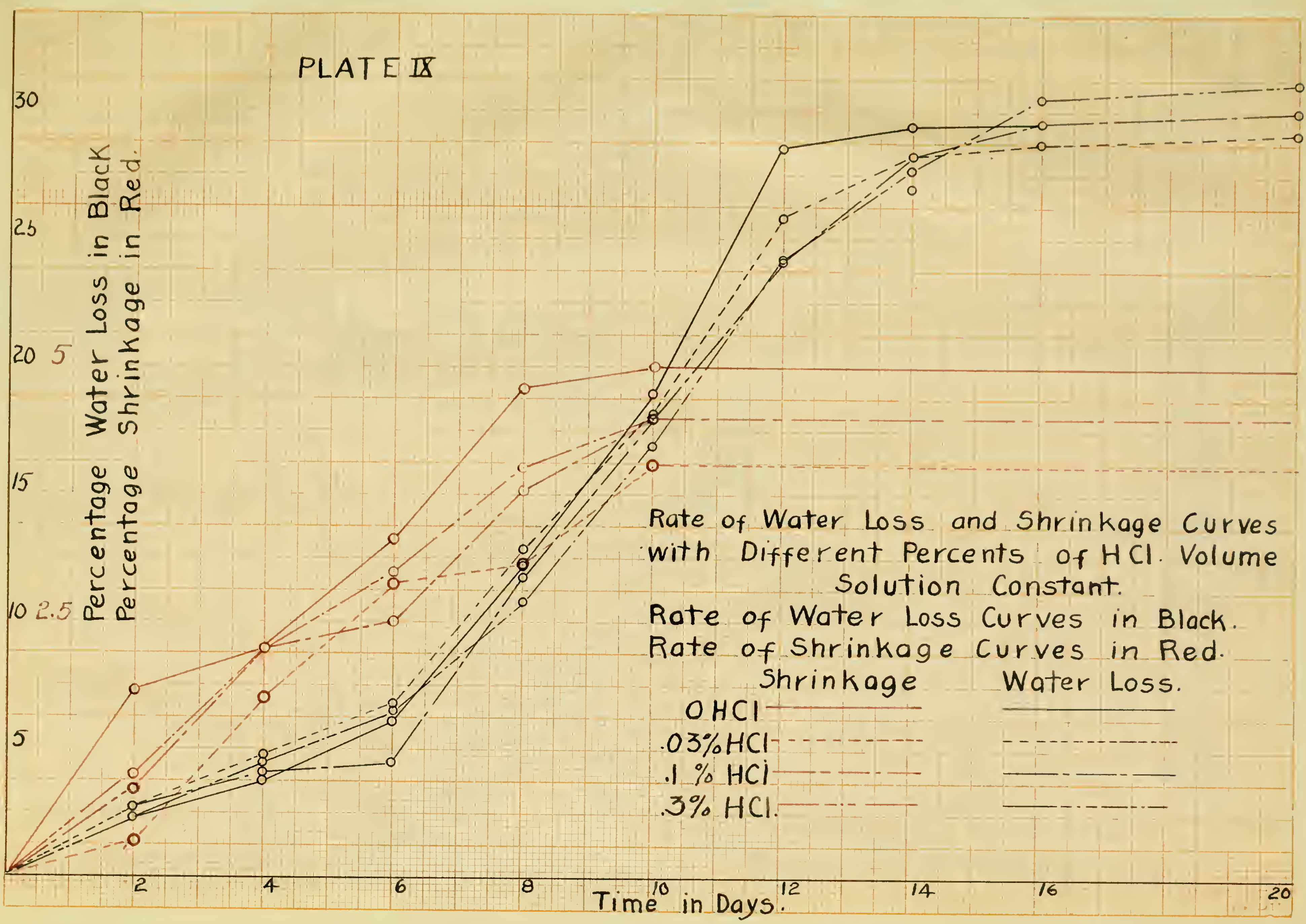
The addition of 2.5 percent of all salts used, with the exception of $MgSO_4$ showed decrease in the rate of drying, although in the latter there was a small decrease. Therefore, the rate of drying decreases as the amount of soluble salts increases. This phenomena was more noticeable in the case of highly deliquescent salts than in those that do not take up water so readily. Thus $MgSO_4$ does not absorb water so fast as the others and reduces the rate of drying less. In the case of soluble salts it is probable that the cause of slower drying is due to the salts robbing the colloids of the water and thus causing a coagulation of the sols.

The acid electrolytes (PLATES 9 and 10) showed a marked difference in the rate of drying compared with salts. The addition of large percents of acid, 2.5 percent in the case of

$H_2C_2H_3O_2$ and,3 percent of HCl showed very little difference in drying behavior from ball clay and water alone, although these acids are strong coagulators. This effect may be due to the various compounds formed by the acids within the clay and also, that naturally these do not hydrolyze.

These results show that in order to increase the viscosity of slips and indirectly the plasticity of clay without increasing the time of drying,acids are preferable to soluble salts. Also to regulate the drying of slips on single burned ware so that flaking or cracking will not result, soluble salts may be added advantageously and will decrease the rate of drying.

PLATE IX


Rate of Water Loss and Shrinkage Curves with Different Percents of HCl. Volume Solution Constant.
Rate of Water Loss Curves in Black.
Rate of Shrinkage Curves in Red.
Shrinkage
Water Loss.
0 HCl
.03% HCl
.1 % HCl
.3% HCl.
Percentage Water Loss in Black
Percentage Shrinkage in Red.
30
25
20
5
15
10
2.5
5
2
4
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8
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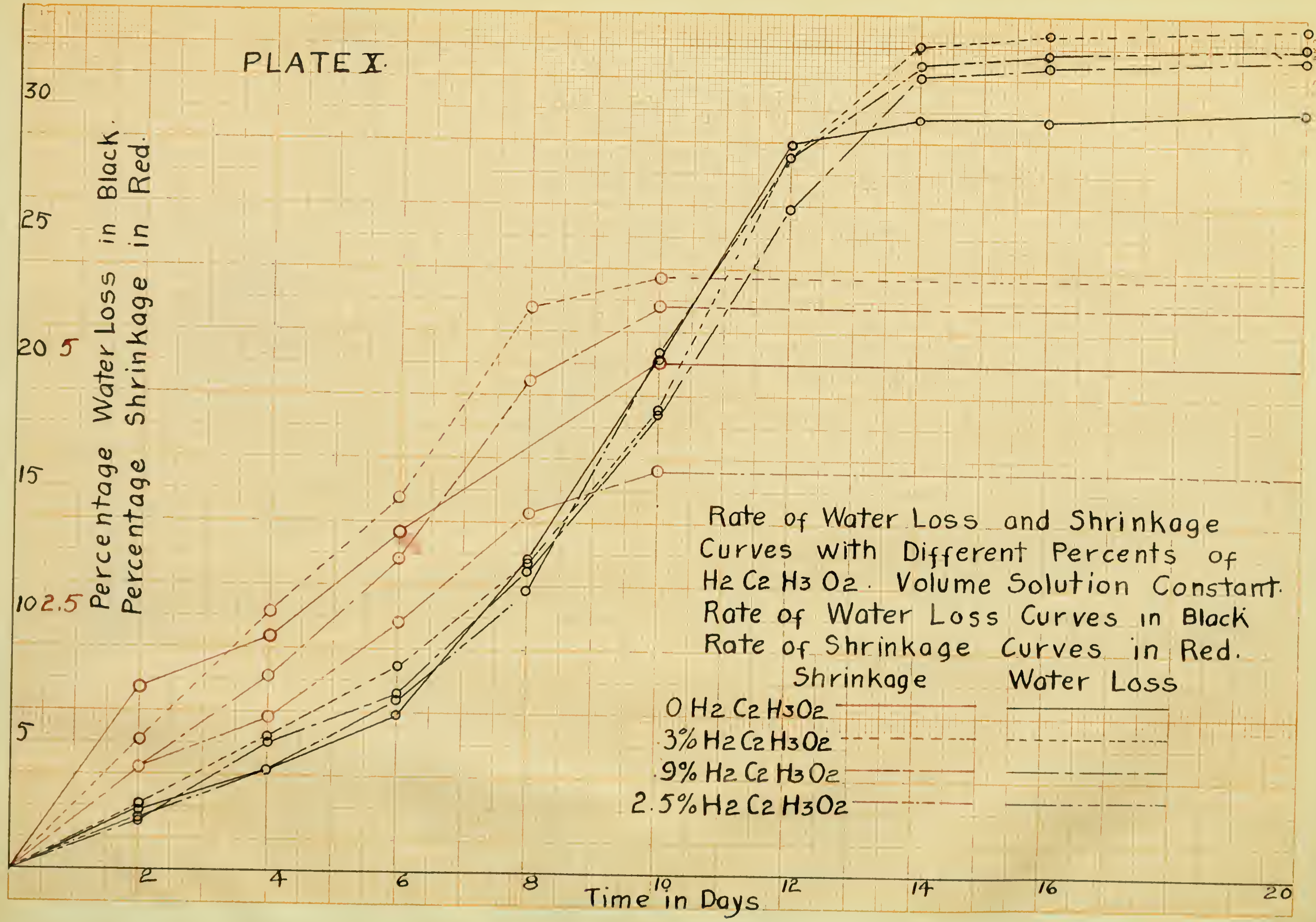
20
Time in Days.

[illegible]

PLATE X.



Rate of Water Loss and Shrinkage Curves with Different Percents of $H_2C_2H_3O_2$. Volume Solution Constant. Rate of Water Loss Curves in Black. Rate of Shrinkage Curves in Red.

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